

originally resident in the biomass into the final fuel product. Hydrothermal processing also facilitates reuse of nitrogen (N) and phosphorus needed for a sustainable process.

Hydrothermal conversion of biomass to fuels was described in the 1940s (7), and Shell developed a hydrothermal upgrading process in the 1980s (5). Approaches being developed for making fuels from wet algal biomass generally either first complete chemical conversion of the whole biomass and then separate the product fractions, or first fractionate the biomass and then convert the lipid fraction into fuel (see the figure). Hydrothermal treatment of algal biomass at temperatures of ~200°C generates carbonized solids (hydrochar) that can be filter-separated from water and contain nearly all of the lipids (8). The lipids exist as free fatty acids and mono-, di-, and triglycerides; the relative amounts depend on the extent of hydrolysis. The hydrochar can be dried and used directly as a solid fuel (9), or the lipids can be converted to biodiesel fuel by reacting the carbonized solids, either wet or dried, with an alcohol in a process called *in situ* transesterification.

Traditional base-catalyzed transesterification is not suitable because the hydrochar contains fatty acids that would form soaps. Acid-catalyzed transesterification is slower and typically requires higher temperatures than base-catalyzed reactions. Levine *et al.* (8) demonstrated that *in situ* transesterification proceeds readily in supercritical ethanol with no added catalyst and has promise as a route to biodiesel. Direct supercritical transesterification of lipids in freshly harvested wet algal biomass without any prior carbonization step has also been attempted, but the high moisture content [>90 weight (wt) %] presents challenges (10).

Hydrothermal treatment of algal biomass in liquid water at a higher temperature (~300° to 350°C) produces a viscous crude bio-oil that can contain 60 to 80% of the heating value of the biomass (4, 5, 11). This biocrude has a hydrogen to carbon ratio similar to that of the vacuum gas oil cut of a heavy petroleum crude oil, but it is richer in heteroatoms [N at ~3 to 5 wt % and oxygen (O) at ~8 to 10 wt %] that are unwanted in final products and that would not be removed if coprocessed with crude oil.

The biocrude from hydrothermal liquefaction can be upgraded thermally (12) or catalytically (13) to produce a crude bio-oil that is free-flowing at room temperature and has a reduced total heteroatom content. Removal of N atoms from the oil remains a challenge. This hydrothermal liquefaction path to renewable liquid fuels

does not require algae with a high lipid content, although such algae do tend to produce higher yields of crude bio-oil.

Hydrothermal treatment of algae at higher temperatures (e.g., 400° to 600°C) and pressures (e.g., 25 MPa) converts wet algal biomass to gaseous products that are useful as fuels or chemicals. Gasifying part of the algal biomass entering the biorefinery could provide CH₄ for thermal energy and H₂ for catalytic processes such as hydrotreating, hydrocracking, or hydrogenation. Supported ruthenium catalysts have achieved complete gasification of the carbon in algae (14, 15), but catalyst deactivation presents challenges.

The high N content in algal biocrudes from hydrothermal liquefaction, and the potential economic value of proteins and amino acids in some algae species, have motivated work on the extraction of these coproducts. Moscoso and Kumar report that proteins or amino acids can be extracted from algal biomass in subcritical water on a time scale of seconds (16); the balance of the biomass can then be converted to biocrude or biodiesel. Likewise, polysaccharides can be extracted hydrothermally from algae and the extracted biomass then liquefied to make bio-crude (17).

Supercritical CO₂ has been used to remove lipids first from wet algal biomass (18) at temperatures of ~100°C, which are lower than those used for hydrothermal extraction and processing, but the optimal pressure is much higher (e.g., 40 MPa). Moreover, the

conditions used are far from the critical point of CO₂, so some of the solubility advantages of supercritical fluid extraction vanish.

Finally, it is likely that optimal processing conditions will vary with the biochemical content of the alga. Research is moving toward elucidating the chemistry of biomolecules in these rich and complex reaction systems.

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PLANETARY SCIENCE

The Origin of the Moon

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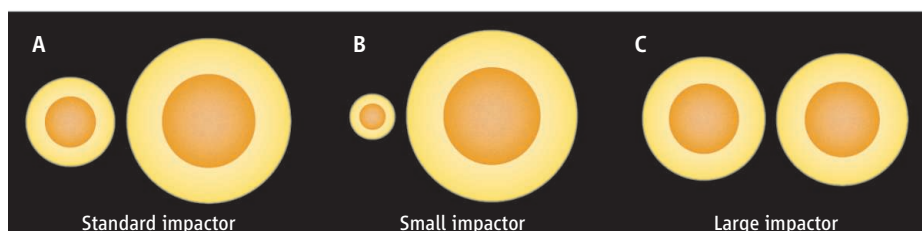
Model simulations provide a new picture of how the Earth-Moon system may have formed.

The Apollo program radically changed our understanding of the origin of Earth and the Moon. The return of a large number of samples for analysis, allowing the determination of isotopic, chemical, and mineralogical compositions of lunar rocks, resulted in a “scientific giant leap” and also posed a particular challenge. Samples from the Moon have primordial isotopic compositions identical to those of Earth, whereas current models predict that they should be distinct, like other solar system

materials. On pages 1047 and 1052 of this issue, Ćuk and Stewart (1) and Canup (2) provide simulations that offer differing solutions to the problem.

Any successful model of lunar origin has to explain the Moon’s angular momentum and its slightly lower density (than Earth). With the return of samples, a number of other constraints became apparent. First, the Moon formed relatively late given its size. Tungsten isotopic data (3) require that the Moon formed more than 30 million years after the start of the solar system, whereas most objects this size are predicted to have formed in the first few hundred thousand years (4). Second, the oldest rocks appear to have

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Collision scenarios. Examples of the three new models of the Moon-forming Giant Impact, each of which allows more angular momentum to be lost and thereby achieves oxygen isotopic compositions that cannot be resolved between Earth and the Moon. (A) “Standard” impactor, 10% of Earth’s final mass, works with “hit and run” collision (14). (B) “Small” impactor, 2.5% of Earth’s final mass (1). (C) “Large” impactor, 45% of Earth’s final mass (2).

formed from a magma ocean (5), implying an intensely energetic fiery start at a time when heat-producing short-lived nuclides (^{26}Al and ^{60}Fe) were extinct. Third, the oxygen isotopic composition of the Moon is identical to that of Earth (6) to within 5 parts per million, whereas that of nearly all asteroidal and planetary objects are different.

The Giant Impact Theory is the resultant widely accepted current explanation for the Moon’s late, molten start as a low-density object that now contributes most of the angular momentum in the Earth-Moon system. Following an early similar model (7), dynamic models using smooth particle hydrodynamic code have been deployed (8, 9) to track the temperature and fate of silicate and dense iron metal resulting from the oblique collision of two planets. In most models, this has been an Earth when it was about 85 to 90% formed and another planet, sometimes called Theia, that was about 10 to 15% of the mass of Earth or roughly the size of Mars (see the figure, panel A). Simulations of this catastrophic glancing blow show that most of the material from Theia was added to Earth, with a small fraction of silicate-rich material left as a disk from which the Moon accreted.

In nearly all “successful” Giant Impact simulations, the material that ends up in the Moon is mainly derived from Theia. To account for the identical isotopic composition, it was proposed that Theia and Earth must have formed at similar heliocentric distances—but then it is difficult to explain why the Giant Impact was so late. Perhaps at the high temperatures achieved during the Giant Impact, Earth’s mantle and lunar accretion disk would have remained in vapor and liquid form long enough to achieve isotopic equilibration by mixing and diffusion (10). This would work for elements as volatile as oxygen. However, refractory elements such as tungsten and titanium are also isotopically identical (3, 11). Further mixing of refractory elements might have occurred during rainout of condensates (12). However, the identical

silicon isotopic composition of Earth and the Moon (13) is not readily explained; the rain-out process is expected to generate a silicon isotopic difference, so the problem persists.

The papers by Ćuk and Stewart and by Canup remove the major constraint that the initial angular momentum was generated by the Giant Impact. Ćuk and Stewart propose instead that after the Moon formed the system was rotating far faster, that Earth could also have been doing so beforehand, and that it has been slowed subsequently as a consequence of a resonance in tidal forces with the Sun. This opens up the possibility of different impact scenarios. Earth itself could have been left spinning rapidly after its prior accretion history, such that a relatively small proportion of the angular momentum of the Earth-Moon system today is the result of the Giant Impact. Without this constraint, it is then possible to investigate a broader array of impact scenarios, and this is where the two papers diverge.

Ćuk and Stewart investigate solutions with a relatively small Theia (less than 10% of Earth’s mass) and a pre-impact angular momentum two to three times that of today. In one example with a mass of Theia of only 2% of Earth’s final mass (see the figure, panel B), they achieve formation of a lunar mass of material in orbit with only 8% being derived from Theia, which compares with a final Earth with as little as 2%. This small proportion of impactor material in both objects limits the possibilities for there being Earth-Moon isotopic differences.

Canup goes to the opposite extreme with models exploring the possibility that Theia was 30 to 45% of the current Earth (see the figure, panel C). As Theia gets bigger, the proportions of the proto-Earth:Theia mix become closer in the two objects. The result is tested using assumptions of isotopic diversity, the strongest constraint for which comes from oxygen that a Theia of more than 40% of the total mass appears to satisfy.

Another class of models has been proposed simultaneously (14), arguing for very

energetic hit-and-run collisions between a Theia with the more conventional 10% Earth mass and removal of angular momentum by loss of material from the system (see the figure, panel A). As with the Ćuk and Stewart model, most of the material in the Moon is derived from the proto-Earth.

Distinguishing among these three models is going to involve further simulation and debate. Geochemical constraints may again prove decisive in three ways.

First, tungsten isotopes are sensitive to equilibration between incoming metal from the impactor’s core and tungsten in the silicate Earth (15). Such equilibration will vary with impact angle (16) and should lead to different isotopic compositions between silicate Earth and Moon after further post-impact equilibration and core formation. This will be less of an issue with a small impactor.

Similarly, the silicon isotopic composition of Earth and the Moon are identical (13), and this is a signature of high-pressure core formation that has been transferred to the Moon. If there is a major increase in the size of Earth, as in the Canup model, it might be expected to further fractionate silicon isotopes relative to the Moon.

Finally, for the particularly energetic models (2, 14), this would be expected to lead to widespread melting and mixing. Yet recent results (17) provide evidence of deep reservoirs with noble gas isotopic heterogeneities that have been preserved since about the time of the Giant Impact. It is not known whether these are localized or widespread, but their presentation is intriguing in a planet that supposedly was built by repeated highly energetic accretion.

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